Laser Cleaning applied on a silver *Carlino* coin

F. Adducci[(1)], A. Buccolieri[(2)], G. Buccolieri [(2)], A. Castellano[(2)], A. Lorusso [(3)], V. Nassisi [(3)], F. Vona [(4)]

[(1)] Department of Physics, University of Bari
[(2)] Department of Material Science, University of Salento, INFN, 73100 Lecce-I
[(3)] Department of Physics, Laboratorio di Elettronica Applicata e Strumentazione LEAS, University of Salento, INFN, 73100 Lecce-I

INTRODUCTION

Nowadays the conservation of cultural heritage and in particular of metallic artefacts is of large importance due mainly to the growth of the environmental contamination. In fact the development of industrial activities and the population growth have caused a remarkable increase of atmospheric pollution, especially in urban areas. Due to above conditions, the dynamics of natural alterations have been accelerated in all the manufactured objects exposed to atmospheric agents. For these reasons, it is necessary to intervene by means of new technology systems of low ambient impact in order to stop the contamination and to restore the artefacts. Generally silver artefacts present on its surface a *patina* but even other metal artefacts present corrosive layers.

Recently, UV laser beam applications in the cultural heritage field are becoming more and more commune. The first cleaning tests using laser beams were performed in the 1970s giving very promising results [1]. Since the first experiences, scientists and conservators have doing much research to investigate the use of lasers as a special cleaning tool. Next, due to technological progresses achieved in the field of power lasers and their great marketing and diffusion, new frontiers in the study of pulsed laser etching and ablation have been opened [2, 3] employing pulsed lasers such as excimer lasers, Nd-Yag lasers, Er-Yag lasers, frequency doubled Nd-Yag lasers and frequency triple Nd-Yag lasers [4, 5]. In the 1997 a pulsed CO_2 laser was used to investigate samples of various metals demonstrating that laser cleaning technique is effective in removing organic paints and stains without damaging the bulk metal [6].

It is well known in fact that pulsed laser beams, of opportune fluences applied to target surface, can operate etching of material by fast and controlled vaporisations of few layers. So this straightforward technique can reach meaningful results in the cleaning field reducing the risk of damaging of artefacts. Otherwise the laser cleaning result depends by many processes which involve the irradiation conditions and the artefact compounds. Consequently, the results of laser application are not always satisfactory, producing in some cases side-effects, such as changes in the colour and in the chemical composition of corrosion products. These investigations demonstrated the complexity of the phenomena involved in laser–metal interaction, pointing out that the laser cleaning has to be used with extreme carefully and evaluating separately ever particular case.

In this work we focus our activity to study the laser cleaning of artefacts made of silver and silver/copper alloy with particular attention to an ancient coin, *Carlino* coined in 1689 under the domination of King Carlo II of Spain.

THEORY

Lasers beams can be applied in the field of the cultural heritage, but it is indispensable to study carefully the process in order to determine the best conditions of irradiation: etching of patina or layer and protection of the bulk.

According to the laser parameters, the photoablation can be induced by three kinds of photoinduced phenomena: Photochemical processes (direct bond breaking and photodissociation); photothermal processes (evaporation by heating and heat conduction) and photomechanical processes (photoionization, plasma formation, fast expansion and shock wave propagation). Depending on the properties of the sample and on the irradiation conditions, such as wavelength and pulse duration, one of them may become dominant.

The heating region depends on the waveform and time duration of the laser pulse and on the thermal diffusion length, z_{th}, which is linked to the heating propagation by the following equation:

$$z_{th} = \sqrt{2k\tau} \qquad (1)$$

where k is the heat diffusivity and t is the laser pulse duration. Therefore, using short duration laser pulse, the heating propagation becomes negligible as well as the depth of the layer which could be ablated.

The photomechanical effect is represented by the mechanical coupling coefficient, C_m, which is described by the equation (2) [7]:

$$C_m = \frac{Pa}{I} \qquad (2)$$

where Pa is the explosion pressure produced by the shock wave provoked by the laser beam and I is the laser intensity. Therefore, by the above considerations, it is difficult to determine *a priori* the best irradiation conditions in laser cleaning of coins exhibiting black layers. So it is noteworthy to say that the region of laser cleaning can be controlled mainly by the laser wavelength, laser energy, pulse duration and target material.

In this work, preliminary results about the laser cleaning on silver and silver/cupper will be reported by using a laser operating in the UV range.

EXPERIMENTS AND RESULTS

For this study, we used a KrF laser operating at 248 nm, 30 ns pulse to process silver artefacts. The beam was focused by a 50 cm focal length lens up to increase the energy density to perform studies on threshold value of the specimens. Instead, the laser cleaning was performed irradiating the samples by a uniform laser beam of about one centimetre square. To reach on good uniformity a transversal filter of 1.5x2.6 mm^2 placed on the focus plane of the lens was used and the samples were placed just 30 cm after the filter.

In order to evaluate the variation of the elements and silver percentage during the different steps of laser cleaning treatment a portable apparatus for Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer and a X-Ray Diffractometer spectrometer (XRD) were used. The characteristics of the EDXRF and XRD instrumentation are described in the references [8-10]. This last was necessary to understand the chemical compounds present on the surface.

The preliminary analyses on coin surface relieved a concentration of sulphur forming the acanthite, Ag_3CuS_2, Fig. 1. We ascribed the black look of the coin to this compound.

Before to removal the layer film without to damage the bulk, it was necessary to operate below the ablation threshold conditions just of the bulk. They were determined experimentally in the following way: we utilized certified silver and silver/copper samples having a flat area and we applied 50 laser shots in different position of different laser pulse energies. In all cases, ablation of material was observed with the formation of craters with the edge raised. Therefore the ablation threshold was calculated by the ablation rate obtained by the cra-

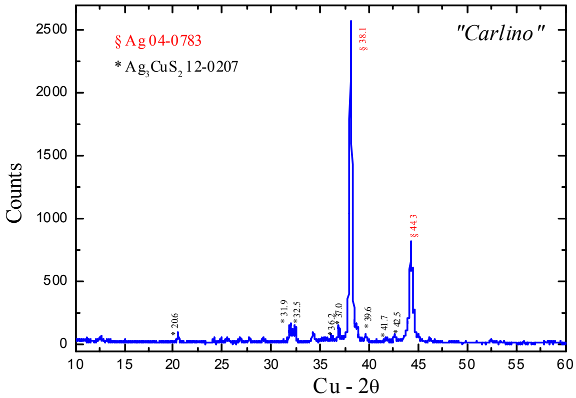

Fig. 1. XRD spectrum of the *Carlino* coin.

ter depth as a function of the total laser dose. The craters due to laser irradiation were characterized by "*Off line*" measurements of the ablated material by utilising a stylus surface profiler (Tencor Instruments ALPHA-STEP 200). Fig. 2 shows a typical result of the profiler obtained by KrF laser for a total laserdose of 3.9 J/cm^2 for the Ag sample.

The crater depth was measured with respect to original plane area. Fig. 3 and Fig. 4 show the ablation rate for the Ag and Ag/Cu samples respectively. In both case the fit of the experimental data points out threshold values of (780±50) mJ/cm^2 and (510±60) mJ/cm^2 for the Ag and Ag/Cu alloy, respectively. To reproduce the same conditions of the coin surface, we created synthetically the sulphur compounds on both samples. So, we exposed the original Ag and the Ag/Cu samples to S acid vapour.

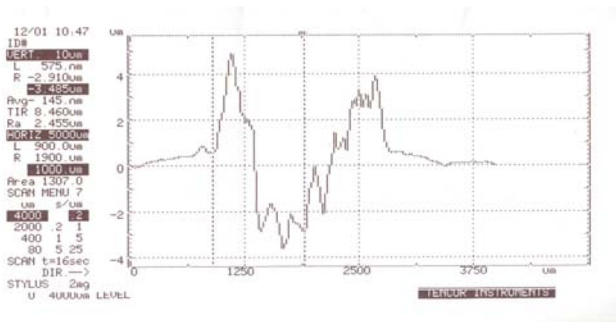

Fig. 2. Typical result of the profiler (all dimensions are in μm).

Ag samples

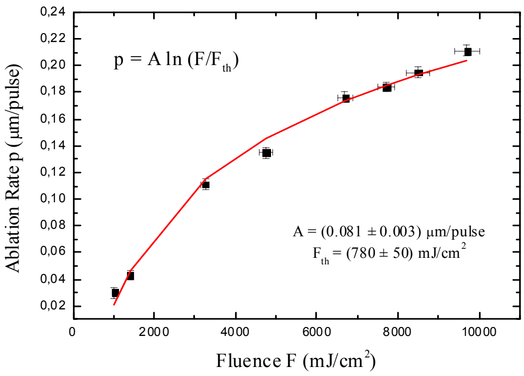

Fig. 3. Etching rate of Ag sample as a function of the laser fluence.

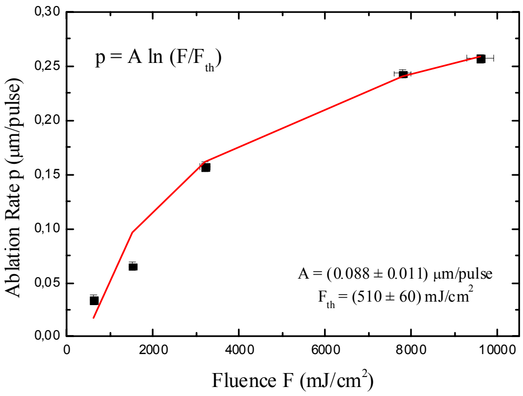

Fig. 4. Etching rate of Ag/Cu sample as a function of the laser fluence.

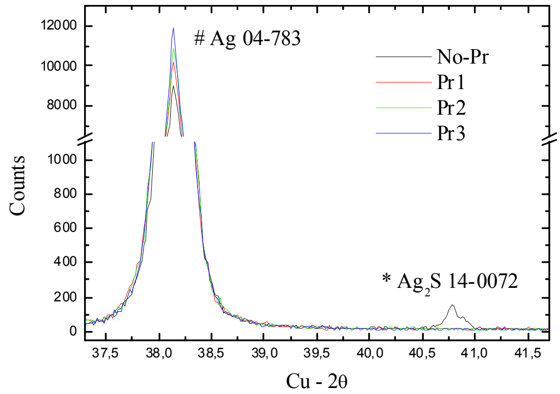

Fig. 5. XRD spectrum of the Ag sample before and after UV laser cleaning. Pr: processing.

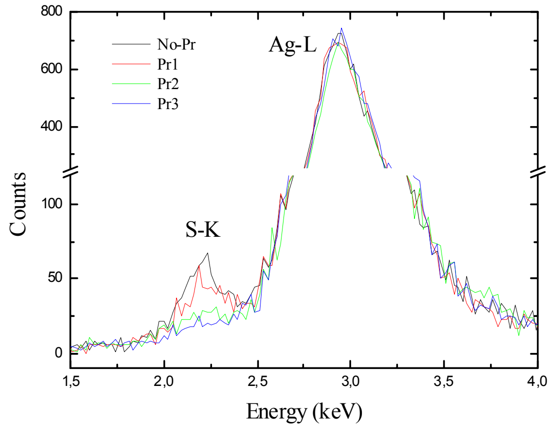

Fig. 6. EDXRF spectrum of the Ag sample before and after UV laser cleaning. Pr: processing.

By the XRD analyses on the silver samples we found the formation of acanthite, Ag_2S.

The laser cleaning action was performed at an energy density less than 200 mJ/cm^2 applying different shots in different steps. For each step the sample was moved in order to illuminate uniformly the whole surface. After ever step XRD and EDXRF analyses were performed. Table I reports the experimental conditions and the sulphur concentrations as well the determinate laser dose.

Fig. 5 shows the XRD spectrum. From these data it is evident the acanthite peak before and after UV laser cleaning for Ag sample, while from Fig. 6, EDXRF spectrum, it is evident the sulphur peak before and during laser cleaning. Both peaks decrease on laser dose. By experimental results of Fig. 6 we determined the decreasing percentage of sulphur by obtaining Fig. 7.

Ag/Cu samples

In this case by the XRD analyses on the sample we found the formation of a new compound, jalpaite Ag_3CuS_2, apart from acanthite.

Again in this case, the laser cleaning action was performed at an energy density less than 200 mJ/cm^2 per laser shot applying different shots in different steps. Every in this case the sample was moved as in previous case. After each step XRD and EDXRF analyses were performed. Table II reports the experimental conditions and the sulphur

	Energy (mJ)	Spot (cm^2)	Laser dose (J/cm^2)	% S (w/w)
Blank			0	6.8±0.9
Processing 1	35.8	0.36±0.02	1.9±0.2	5.8±0.9
Processing 2	298	1.30±0.03	22.5±1.2	2.0±0.6
Processing 3	325	1.23±0.03	25.0±1.4	1.0±0.5

Table I. Experimental conditions and the sulphur concentrations for Ag sample.

concentrations as well the determinate laser dose.

From Fig. 8, where the XRD spectrum is shown, it is evident the presence of jalpaite and acanthite peaks, while Fig. 9 shows sulphur peak. In this last figure it is possible to observe that the S concentration increases with the increase of the laser dose up to 50 J/cm^2 and decreases for higher doses. This result can be ascribed to the photochemical process at low dose which induce the conversion of the acanthite in jalpaite.

From Fig. 8 it is clear that for low laser doses (<50 J/cm^2) dominate the effects of conversion of acanthite in jalpaite being this last more stable and as a consequence we have an enrichment of sulphur concentration. For higher doses the sulphur is removed. Fig. 10 shows the sulphur concentration versus laser dose for an Ag/Cu sample processed by UV laser.

Carlino sample

By the XRD analyses on the coin surface we found the formation of jalpaite, Ag_3CuS_2.

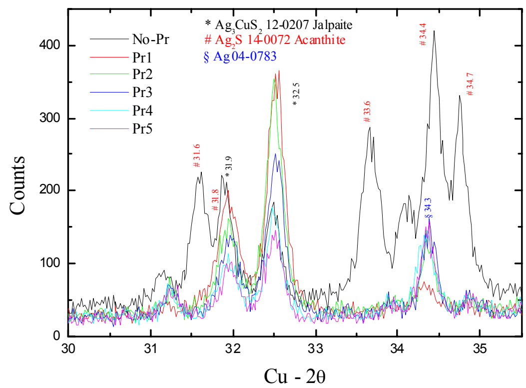

Fig. 8. XRD spectrum of the Ag/Cu sample before and during UV laser cleaning.

The laser cleaning action was performed at an energy density less than 200 mJ/cm^2 applying different shots in different steps. After each step XRD and EDXRF analyses were performed. In particular, EDXRF analyses were performed on four different region of coin. In all the regions of the sample the sulphur concentration decreases on total laser dose of the same percentage, Fig. 11.

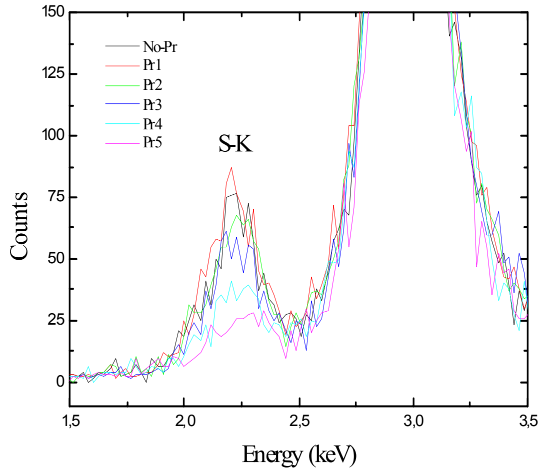

Fig. 9. EDXRF spectrum of the Ag/Cu sample before and during UV laser cleaning.

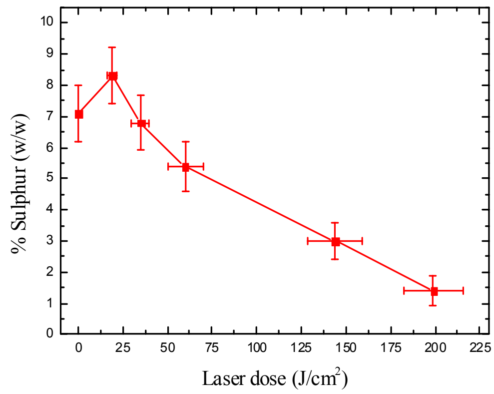

Fig. 10. Sulphur concentration versus the laser dose for an Ag/Cu sample processed by UV laser.

Finally we processed the Carlino by a fluence of 150 mJ/cm^2 and different laser shots. Operating on the coin up to a dose of 280 J/cm^2 the sulphur concentration deceases up to 20 %, while the coin became look clear just after a 50 J/cm^2. Fig. 12 shows the coin surface at 50 J/cm^2 a) and at 200 J/cm^2 b).

	Energy (mJ)	**Spot (cm^2)**	**Laser dose (J/cm^2)**	**% S (w/w)**
Blank			0	6.5±1.0
Processing 1	306	1.33±0.03	19.2±1.0	8.3±1.0
Processing 2	285	2.12±0.03	15.5±0.8	6.8±0.9
Processing 3	275	1.78±0.03	25.6±1.3	5.4±0.8
Processing 4	267	2.12±0.03	84±4	3.0±0.6
Processing 5	259	1.97±0.03	55±3	1.4±0.5

Table II. Experimental conditions and sulphur concentrations for Ag/Cu sample.

CONCLUSION

Experimental results about the laser cleaning of Ag/Cu coins show that the pulsed lasers can be used safety as a powerful tool to remove the *patina*

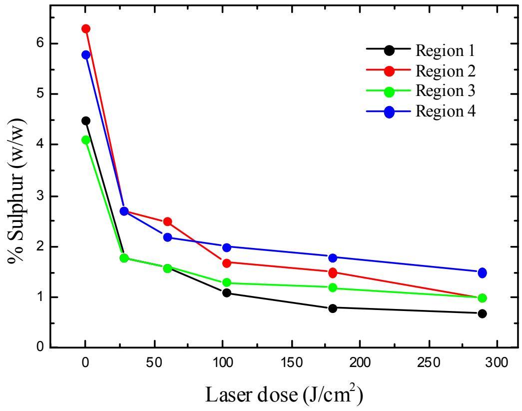

Fig. 11. Sulphur concentrations vs laser dose for different regions of coin.

of silver coins. Operating below the threshold laser fluence, the UV laser actions is able to remove the patina from the surface of the coins more than 80 %. Besides, the obtained results prove that UV laser cleaning is able to preserve the bulk of the coins. Moreover the more meaningful result, observed for the first time, was the photochemical action at low dose which induce the conversion of

Fig. 12. *Carlino* coin during UV laser processing.

the acanthite in jalpaite.

REFERENCES

[1] Asmus J.F., *Light cleaning: laser technology for surface preparation in the arts,* Technology Conservation (1978) 14-18.

[2] Salimbeni R., Pini R., Siano S., *A variable pulse width Nd:YAG laser for conservation*, Journal of Cultural Heritage 4 (2003) 72-76.

[3] Siano S., Salimbeni R., Pini R., Giusti A., Matteini M., *Laser cleaning methodology for the preservation of the Porta del Paradiso by Lorenzo Ghiberti*, Journal of Cultural Heritage 4 (2003) 140-146.

[4] Pini R., Siano S., Salimbeni R., Pasquinucci M., Miccio M., *Tests of laser cleaning on archeological metal artefacts*, Journal of Cultural Heritage 1 (2000) S129-S137.

[5] Drakaki E., Karydas A.G., Klinkenberg B., Kokkoris M., Serafetinides A.A., Stavrou E., Vlastou R., Zarkadas C., *Laser cleaning on Roman coins*, Appl. Phys. A 79 (2004) 1111-1115.

[6] Cottam C.A., Emmony D.C., Larson J., Newman S., *Laser in Conservation of Arteworks*, (LACONA II), Restauratorenblätter (Special issue), Mayer & Comp., Vienna, 1997.

[6] Scott D.A., *Copper and Bronze in Art*, Getty Pubblications, Los Angeles, 2002.

[7] Lee J.M., Watkins K.G., *Removal of small particles on silicon wafer by laser-induced airborne plasma shock waves*, J. Appl. Phys. 89 (2001) 6496-500.

[8] Cesareo R., Castellano A., Buccolieri G., Quarta S., Marabelli M., *Giotto in the Chapel of the Scrovegni: EDXRF analysis of the golden haloes with portable equipment*, X-Ray Spectrometry 33 (2004) 289-293.

[9] Castellano A., Buccolieri G., Quarta S., Cesareo R., Marabelli M., Santopadre P., Ioele M., Gigante G.E., Ridolfi S., *Cultural Heritage Conservation and Environmental Impact Assessment by non-destructive testing and micro analysis*, A.A. Balkema Publishers, London, 2005.

[10] Buccolieri G., De Stefano L., De Luca F., Plescia P., *Milling effects upon quantitative determinations of chrysotile asbestos by the reference intensity ratio method*, Powder Diffraction, 15 (1), 26-29, March 2000.